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THE PERIODIC TABLE – ITS FORMALIZATION, STATUS, AND RELATION TO ATOMIC THEORY*

“...I tried to explain...that...Mendeleev’s Periodic Table, which just during those weeks we were laboriously learning to unravel, was poetry, loftier and more solemn than all the poetry we had swallowed down in liceo; and come to think of it, it even rhymed!” (Primo Levi, *The Periodic Table*, p. 41)

1. INTRODUCTION

In this paper a formalization for the Periodic Table of elements is given, following the structuralist approach. Moreover, the relation between Atomic Theory and the Periodic Table is investigated, using the formalization of the Periodic Table.

We start with a short historical introduction into the matter in Section 2. Then we present our formalization for the Periodic Table in Section 3. We assume that the reader is familiar with the main concepts of the structuralist approach (Balzer, 1982; Balzer and Sneed, 1977, 1978; and Sneed, 1971). We obtain a naive and a sophisticated version of the Periodic Law and hence of the Periodic Table.

In Section 3 we deal with the relation of the Periodic Table to the physicist’s Atomic Theory. It is claimed that the physicist and the chemist have a different conception of the atom, that the original version of the Periodic Table is based on the chemist’s conception, and that the conception of the physicist, based on the Atomic Theory, has gradually taken its place. However, this does not exclude, on the contrary, that the formal structures, in particular the potential models, remain essentially the same. This makes it possible that Atomic Theory can explain (and even reduce) the chemist’s formulation of the sophisticated Periodic Law. We will not describe this reduction in structuralist detail, although this might lead to interesting new insights. We will confine ourselves to showing that the present case of

PERIODIC TABLE OF ELEMENTS

Atomic weights are the most recent (1961) adopted by the International Union of Pure and Applied Chemistry. The numbers are all relative to the atomic weight of the principal isotope of carbon, C^{12} , defined as exactly 12.00000. For artificially produced elements, the approximate atomic weight of the most stable isotope is given in brackets.

Group →	I	II	III	IV	V	VI	VII	VIII	0
Period	Series	1 H							2 He
1	1	1.00797							4.0026
2	2	3 Li 6.939	4 Be 9.0122	5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
3	3	11 Na 22.9898	12 Mg 24.312	13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
4	4	19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847
								27 Co 58.9332	28 Ni 58.71
	5	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
	6	37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc [99]	44 Ru 101.70
								45 Rh 102.905	46 Pd 106.4

7	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
	107.870	112.40	114.82	118.69	121.75	127.60	126.9044	131.30
8	55 Cs	56 Ba	57-71 Lanthanide series*	72 Hf	73 Ta	74 W	75 Re	76 Os
	132.905	137.34		178.49	180.948	183.85	186.2	190.2
9	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
	196.967	200.59	204.37	207.19	208.980	[210]	[210]	[222]
10	87 Fr	88 Ra	89-103 Actinide series†	104 Rf‡	105 Ha‡			
	[223]	[226]						

*Lanthanide Series: 57 La 138.91 58 Ce 140.12 59 Pr 140.907 60 Nd 144.24 61 Pm [147] 62 Sm 150.35 63 Eu 151.96 64 Gd 157.25 65 Tb 158.924 66 Dy 162.50 67 Ho 164.930 68 Er 167.26 69 Tm 168.934 70 Yb 173.04 71 Lu 174.97

†Actinide series: 89 Ac 227 [227] 90 Th 232.038 [231] 91 Pa 231 [231] 92 U 238.03 [237] 93 Np 237 [237] 94 Pu 242 [242] 95 Am 243 [243] 96 Cm 245 [245] 97 Bk 249 [249] 98 Cf 249 [249] 99 Es 253 [253] 100 Fm 255 [255] 101 Md 256 [256] 102 No 257 [257]

‡ Proposed symbols for Rutherfordium (Rf) and Hahnium (Ha). See A. Ghiorso, *Science*, Vol. 171, p. 127 (1971).

Source: From Appendix IV of Holton (1973), p. 541.

reduction is a particularly interesting illustration of an informal decomposition-model of reduction.

In Section 5 we discuss the most fundamental question of this paper whether the Periodic Table is a proper theory or merely an empirical law. Our conclusion is that it started as a proper theory, with atomic numbers as a theoretical function, but that (the sophisticated version of) the Table turned *in principle* into an empirical law, with the Atomic Theory as an underlying theory that identifies the atomic number as the number of electrons.

In our opinion, Section 5 is a representative example of the advantages of the structuralist formalization. The 'model-perspective' does not only fundamentally differ from the traditionalist 'statement-perspective', it brings moreover in the right middle between informal statement formulation and formal statement axiomatization. Our formalization is just enough to answer the fundamental question of the epistemological status of the Periodic Table, leading to an appealing distinction between a *de facto* and *de jure* reconstruction of relations between laws and theories.

For purposes of easy consultation we include here an example of the Periodic Table. We have chosen for the table in Holton (1973). It is not very modern, but for this reason it will look familiar not only to chemists but also to readers with only elementary knowledge of chemistry.

2. HISTORY OF THE PERIODIC TABLE

Although the term 'chemical element' seems not at all problematic at present, this has not always been the case. In ancient times, there was some sort of conception of a 'smallest particle' as a basic ontological entity, but at the same time this conception was the subject of much metaphysical speculation and discussion. In the first instance a non-atomistic concept of 'chemical element' resulted from this discussion by the end of the eighteenth century. By that time, for a chemical element a working definition was being used, which had the following form: 'a chemical element is a substance that cannot be decomposed into other substances by any (chemical or physical) means, available at the present time'. Lavoisier wrote, in his preface to his *Elements of chemistry* (1789):

"... that if, by the term *elements* we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable that we know nothing at all about them; but if we apply the term *elements* or *principles of bodies*, to express our idea of the point which (chemical) analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition. (Holton, 1973, p. 310)

So by this time, the metaphysical discussion had become irrelevant for the empirical investigation of elements, and the first experiments could make a start.

This did not take too long. By the work of John Dalton (1766–1844), who introduced the concept of a 'chemical atom' and thus performed an effective marriage between the term 'chemical element' and the atomistic hypothesis, and by the work of Avogadro (1776–1856), a host of experimental data such as atomic mass became available, and the concept of 'valence' was introduced. These experimental data led to different attempts to find a classification for the elements.

A first attempt was formed by the 'triads' of Doberreiner (1780–1849), who discovered certain regularities in the behaviour of the then known elements. For three elements with the same chemical behaviour, there existed a relationship in the atomic mass, so that the atomic mass of one element was the average of the two others. Thus, for the typical triad Li, Na, K, the atomic mass of Na is the average of the atomic masses of Li and K.

Around 1860 the developments were more rapidly. It is from this time that the attempts of Newlands (1837–1898) and de Chancourtois (1820–1886) stem. Newlands put the elements in a system much alike to the form we know now, and postulated a 'law of octaves': elements of the same chemical family (that is: that exhibit about the same chemical behaviour) repeated themselves just like the tone 'C' in an octave; after each series of seven or so the chemical behaviour repeated itself. Unfortunately, Newlands put some elements with the same chemical behaviour (chemically similar elements) not correctly with respect to their properties. Also a thorough empirical classification, which Mendeleev was able to give, failed. De Chancourtois proposed to classify the elements in a helix-like structure.

It was the Russian chemist Mendeleev (1834–1907) who formulated the classification now known as the Periodic Table. The central notion of this system is what he called the Periodic Law: when elements are

ordered according to their atomic masses, their chemical behaviour is a periodic function of this ordering.

The first translation of this periodic law into a Periodic Table, contained, however, a few mistakes in the light of the law (Sundaram, 1985). The first formulation of the Periodic Table listed the groups horizontally. At first, the copper group appeared in the first and eighth column, and fluorine appeared above manganese instead of chlorine (see Sundaram, 1985, p. 108). Of course, Mendeleev later altered his original table, to create a version that avoided these errors. This version of the Periodic Table is very much alike the version printed here.

In his 1879 article 'The Periodic Law of Chemical Elements' Mendeleev used his latest table for the following:

- (i) classification of elements
- (ii) giving a systematic account of the properties of already known compounds
- (iii) determination and correction of the atomic masses of (especially little known) elements
- (iv) prediction and examination of the properties of unknown elements (like Ge) and their compounds.

Of these, especially (iv) led to the quick acceptance of Mendeleev's Periodic Table, because the detailed information Mendeleev was able to give was mostly confirmed every time a new element was discovered, which happened several times in that period. As such, this episode is an excellent illustration of the rule of successful predictions in the acceptance of a new idea.

Here we stop our short history of the Periodic Table. Readers who want to know more about the earlier and later history are advised to consult Shapere (1974), also for further references, and Bensaude-Vincent (1986). The applications (i)–(iv) can be found in Sundaram (1985).

3. FORMALIZATION

3.1. *Potential Models*

In order to construct a potential model of the Periodic Table we postulate first a non-empty, finite set E , representing *the set of chem-*

ical elements. Hence, we assume naively that there exists in some sense a fixed and complete set of elements, but it is hard to specify precisely in what sense, for we want of course to have room for talking about elements which have not yet been discovered at a certain stage and elements which can only be made artificially, etc. Let e , e' etc., indicate arbitrary members of E .

Next we postulate the *atomic mass function* m from E into the positive real numbers \mathbb{R}^+ .

Further we assume the binary (*chemical*) *similarity relation* \sim on E of exhibiting about the same chemical behaviour, or, put in a standard term of the Periodic Table, belonging to the same (chemical) group. This term suggests already that \sim is an equivalence relation, and this will be assumed throughout. The group to which e belongs is then of course the equivalence class $\{e'/e' \sim e\}$.

Finally, we assume the *atomic number function* z from E into the positive natural numbers \mathbb{N}^+ . In order to exclude inessential, isomorphic variants we assume that there is an element having z -value 1 (formally $1 \in \text{Range}(z)$).

In sum, we propose the following definition of a potential model of the Periodic Table:

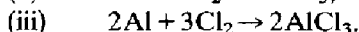
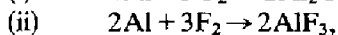
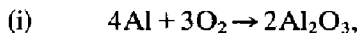
- Df. 1: x is a *potential model* of the Periodic Table
 $(x \in M_p(\text{PT}) \text{ iff there exist } E, m, \sim, \text{ and } z \text{ such that:}$
 (1) $x = \langle E, m, \sim, z \rangle$,
 (2) E is a non-empty, finite set (the set of chemical elements),
 (3) $m: E \rightarrow \mathbb{R}^+$ (the atomic mass function),
 (4) $\sim \subseteq E \times E$, equivalence relation (the relation of chemical similarity),
 (5) $z: E \rightarrow \mathbb{N}^+$ such that $1 \in \text{Range}(z)$ (the atomic number function).

It will be no surprise that we will treat z as the (only) theoretical term. As can be seen in the historical introduction, a conception of a 'chemical element', and hence of a 'set of chemical elements E ' was already existing in an instrumental fashion. No experimental problems arise in the measurement of either the atomic mass function m or the chemical similarity relation \sim .

Measurement of m was possible by making use of the 'ideal gas law'. A 'molar mass', resulting from these experiments proved to be a

unique number for each element, which later could be identified as 'atomic mass'.

An example might be helpful to get a clearer view on the similarity relation: suppose a chemist has got one metal e.g., Al, and some gases, e.g., O₂, Cl₂ and F₂. He decides to let this one metal react with the three types of gas, and from this, to put up the equation for the reactions. Doing this, he finds:



So, in the last two cases, the gases react similarly, while in the first case there is no correspondence to either of the cases: if in all reactions the same amount of gas is taken, then the first reaction uses twice the amount of metal. But suppose our chemist is not yet convinced, and tries to dissolve the three products in water. The first product dissolves, but not too well, while the last two products dissolve very well, thereby producing an irritating gas. So, from these simple experiments one can conclude that the elements F and Cl stand in the similarity relation, and element O is a member of another group, since it does not stand in the similarity relation to either F or Cl. Adding a new group to the ones already known is required when the element under study does not stand in the similarity relation with any thus far known element.

This kind of experimental information was quickly generalized in the concept of chemical 'valency'. Elements standing in the chemical similarity relation were said to possess the same 'valency'. In the above example F and Cl possess the valency 1, whereas the element O possesses valency 2. For an interesting exposition and discussion of stoichiometry and the related concept of 'valency', see Balzer, Moulines and Sneed (1987).

It would, however, be a mistake to view the 'chemical similarity' as being nothing but 'having the same valency'. In fact, chemical similarity has a much broader meaning. It includes also certain regularities in e.g., melting and boiling points of the elements and their compounds. The detailed predictions Mendeleev gave concerning undiscovered elements, dealt, apart from information about the composition of their compounds, mainly with statements about this kind of 'physical' information.

We are left over with the term z as the theoretical term. In Section 5 we will discuss when and in what sense this description of z is adequate.

3.2. *The Periodic Law*

The Periodic Law, the central law of the Periodic Table, runs roughly as follows: when the elements are ordered according to atomic mass, their chemical behaviour, as 'summarized' by the similarity relation, is some periodic function on this sequence. This pattern enabled Mendeleev to design a two-dimensional classification of the elements known to him.

For example, putting atomic masses between brackets, starting with Li the sequence of elements ordered by mass runs according to Mendeleev's information, as follows:

Li(7) Be(9.4) B(11) C(12) N(14) O(16) F(19)

Neglecting inert gases, the next element is Na(23). Because it was known that Na and Li are (chemically) similar he put Na in a new row under Li and continued this row according to the mass-sequence, which gave him:

Na(23) Mg(24) Al(27.4) Si(28) P(31) S(32) Cl(35.5)

The core of periodicity is of course that all the pairs of elements thus occurring in the same column happen to be similar.

We will consider two versions of the Periodic Law (PL). The naive one (NPL) due to Mendeleev and the present-day sophisticated one (SPL) developed in contact with the Atomic Theory. Before we formulate them it is better to discuss some requirements that have to be included in the definition of a model of the Periodic Table. All three requirements directly involve the purported theoretical function z and will turn out to be not completely satisfiable.

To begin with, the leading idea is that z orders the elements according to mass, hence we have at least the following (order preservation or) *monotonicity requirement*:

MR $m(e) < m(e')$ iff $z(e) < z(e')$

Exceptions to MR that have to be accepted will be called *order exceptions*.

Another idea is that z is such that there are no open places, assuming, as we did, that E is indeed complete. Hence, we impose the (onto or) *surjection requirement*, where $\max(z)$ indicates the maximum value of z :

SR z is a surjection in the sense that $\text{Range}(z) = 1, 2, \dots, \max(z)$

Exceptions to SR, i.e. numbers lower than $\max(z)$ for which there is no element in E , will be called (proper) *existential exceptions*.

Finally there was originally the idea that z is a one-one function, hence we get the *injection requirement*

IR z is an *injection* (if $z(e) = z(e')$ then $e = e'$)

Exceptions to IR are well-known as *isotopes*. Isotopes are defined as elements differing slightly in mass, but behaving chemically identical (which is more than merely similar), for which reason they get the same atomic number. It is clear that isotopes are also order exceptions. Moreover, other order exceptions may or may not be due to the 'interference' of isotopes. Hence we may talk about three types of order exceptions: isotopic, due to isotopes, and proper.

Now we can again turn our attention to the Periodic Law. According to Mendeleev, there is a unique periodicity, namely 8 (if we include the inert gases): the 8th element, according to the mass-sequence, before or after a given one is similar to that given one. In terms of atomic numbers Mendeleev's Periodic Law, to be called the naive Periodic Law (NPL), can be formulated as follows

NPL $e \sim e'$ iff $|z(e) - z(e')|$ is a multiple of 8

It is clear that NPL has two predictive aspects, corresponding to the two implications: NPL predicts for two similar elements something about the number of elements in between, and NPL predicts the existence of similar elements at certain 'distances' from a given element.

Mendeleev did not explicitly introduce atomic numbers, but in developing the two-dimensional table, starting from the atomic mass sequence, he left open spaces for not yet discovered elements, just on the basis of his idea that there is a period of 8 elements. Of course, in this way he introduced in fact implicitly the atomic numbers.

It is interesting to mention that Mendeleev expected, next to the

Periodic Law, which is merely an ordering relation between atomic numbers and chemical similarity, a precise quantitative relation between atomic mass and similarity. Later developments did not reveal such a relation, but showed instead that Mendeleev's version of the Periodic Law was untenable.

The modern, sophisticated version of PL, SPL, has to be formulated in two parts, the second one even in two subparts.

SPL-(i) if $e \sim e'$ and $z(e) < z(e')$ then there exists n ($=1, 2, 3, \dots$) such that

$z(e') - z(e) = 2n^2$ or there exists e'' such that $e \sim e''$ (and hence $e'' \sim e'$) and $z(e) < z(e'') < z(e')$;

SPL-(ii) *forward*: for all e there exist e' and n ($=1, 2, 3, \dots$) such that $e \sim e'$ and $z(e') - z(e) = 2n^2$ or there is no similar element after e (i.e., or there is no e' such that $e \sim e'$ and $z(e') > z(e)$),

backward: analogous.

SPL-(i) states and hence predicts that similarity implies that the respective atomic numbers differ some instance of $2n^2$ ($2, 8, 18, 32, \dots$) or that there is some similar element in between (where (i) now applies to the combinations $\langle e, e'' \rangle$ and $\langle e'', e' \rangle$).

SPL-(ii) states and hence predicts that there is always a similar element at a distance of some instance of $2n^2$ after/before a given element if there is a similar one after/before at all. It is easy to check that SPL reduces to NPL if n is fixed at the value 2 (and hence $2n^2$ at 8).

SPL has been developed in close contact with the Atomic Theory. This will be discussed in some detail in Sections 4 and 5. Here we recall only the well-known fact that in Atomic Theory, z gets the interpretation of the number of electrons. Moreover, n , in the expression $2n^2$, corresponds to the so-called 'principal quantum number'.

Of course we define a model of the naive/sophisticated Periodic Table (NPT/SPT) as follows:

Df. 2: x is a *model* of the naive/sophisticated Periodic Table ($x \in M(\text{NPT})/x \in M(\text{SPT})$) iff there exist E , m , \sim , and z such that:

(1) $x = \langle E, m, \sim, z \rangle$ is a potential model of the Periodic Table,

- (2) monotonicity requirement (MR),
- (3) surjection requirement (SR),
- (4) injection requirement (IR),
- (5) naive/sophisticated Periodic Law (NPL/SPL).

3.3. The empirical claim

For the Periodic Table (theory) there exists only one *intended application*, namely the set of chemical elements E . In general, an empirical claim w.r.t. an intended application presupposes the *descriptive claim* that the intended application can be described as a *partial* potential model of the theory. Partial potential models can be obtained from potential models by omitting the (purported) theoretical terms. In our case this is z , hence we get:

Df 3: y is a *partial potential model* of the Periodic Table ($y \in M_{pp}(PT)$) iff there exist E , m , and \sim such that:

- (1) $y = \langle E, m, \sim \rangle$,
- (2) E is a non-empty, finite set (the set of chemical elements),
- (3) $m: E \rightarrow \mathbb{R}^+$ (the atomic mass-function),
- (4) $\sim \subseteq E \times E$, equivalence relation (the chemical similarity relation).

The *descriptive claim* (DC) of PT is that there is an independently measurable function m_E and relation \sim_E such that

$$\langle E, m_E, \sim_E \rangle \in M_{pp}(PT).$$

Let us indicate this description by s_E . Hence

DC there are independent m_E and \sim_E such that
 $\langle E, m_E, \sim_E \rangle =_{df} s_E \in M_{pp}(PT).$

The *empirical claim* (EC) of PT is that s_E can be supplemented with a function z_E such that $\langle s_E, z_E \rangle$ is not only a potential model ($\langle s_E, z_E \rangle \in M_p(PT)$) but even a model ($\langle s_E, z_E \rangle \in M(PT)$). As the latter implies the former it suffices to state as empirical claim of PT

(EC) there is z_E such that $\langle s_E, z_E \rangle \in M(PT).$

Of course we have to distinguish between the claim of the naive theory (ECN) and that of the sophisticated theory (ECS).

Even apart from incidental, local exceptions to the three requirements MR/SR/IR it became gradually clear that there was some structural mistake in Mendeleev's naive theory: though some periodicity was roughly defensible, a constant period (of 8) turned out to be untenable.

Hence, the empirical claim of the naive theory ECN cannot be satisfied, even if local exceptions are allowed. On the other hand, the empirical claim of the sophisticated theory ECS can be satisfied, though only with a number of local exceptions:

IR-exceptions: there are many isotopes, examples of isotopic combinations are: all isotopes of hydrogen (^1H , ^2H and ^3H); all isotopes of potassium (K) with masses in the range of 37–45. An example where the effect of isotopes is considerable is Cl. This element has two isotopes: ^{35}Cl , with natural abundance of 75.77% and ^{37}Cl , with natural abundance of 24.23%; leading to a measurable atomic mass of 35.45.

SR-exceptions: there are a few existential exceptions, examples may be found for higher z values: elements 104, 105, 106 and 107 for instance. These elements do not exist in nature, but are prepared by nuclear reactions. In 1976 the discovery of element 107 was claimed by a Russian group, but this claim was not universally accepted. These elements have very short lifetimes (for instance 2/1000 s), decaying rapidly into other substances.

MR-exceptions: first there are the isotopes as order exceptions; as far as we know there are no order exceptions due to isotopes; finally, an example of a proper order exception is Ar ($z = 18$, $m = 39.948$) and K ($z = 19$, $m = 39.102$).

Before we discuss matters of theoreticity, we turn to the Atomic Theory.

4. ATOMIC THEORY AND THE PERIODIC TABLE

In this section the structural relation between Atomic Theory and the Periodic Table will be considered. It will proceed along the following lines: first, a distinction will be made between the 'chemical' and the 'physical' conception of the atom; next, the relation between the

Periodic Table based on the 'physical' conception and the Periodic Table, based on the 'chemical' conception will be discussed.

4.1. *Two pictures of the atom*

First, we will define what is meant by the term 'chemical' conception of the atom. The '*chemical*' conception of the atom pictures the atom as a basic entity, with certain chemical characteristics, in particular the ability to form molecules with other atoms. On these chemical characteristics the chemical equivalence relation is based. At the time Mendeleev wrote his articles and thereafter, the actual existence of these atoms was still under discussion, and the debates on this subject concentrated mainly on the possibility of an 'atomic theory' being able to account for the behaviour of elements and their compounds as they were seen by the chemists in those days. A little later, 'atoms' were found to exist physically. Early experiments exhibited its structure, which we will hereby define as the '*physical* picture': an atom consists of a heavy nucleus, surrounded by a 'cloud' of electrons.

The structure of this electron cloud can be found by applying quantum mechanical principles, and determines the 'chemical' behaviour. Unfortunately exact solution of a problem involving more than two interacting particles is mathematically impossible. Practically, this means that an exact quantum mechanical solution is only available for the hydrogen atom; even to find a solution for the He atom we have to go into some level of approximation.

Today, a quantum chemist can perform calculations on atoms and molecules on a variety of 'levels of approximation'. The quantitative accuracy of the results is for an important part dependent on the choice of the level of approximation.

In chemistry nowadays there exists a tendency to base qualitative discussions on a highly approximate level of the physical picture of the atom. (In fact, the level of approximation can become so high, that this kind of picture cannot be called 'physical' any longer.) The obtained results, as they emerge out of these qualitative discussions, concern mainly *molecular* properties. Hence, we would prefer to refer to this type of atomic picture as being still a 'chemical' picture of the atom.

The distinction made above is of a crude and intuitive type, and it can be refined in many ways. But we claim that the distinction is still

partially correct. Most chemists still picture an 'atom' not merely as a system of a nucleus and several electrons, but also as inherently a constitutive part of a molecule. So, for our purposes, we can keep up the distinction in the following way: a 'chemical' conception distinguishes itself from the 'physical' picture by being primarily meant to describe the role atoms play in molecules.

4.2. *The relation between the two pictures*

Once we have made the distinction between a 'chemical' and a 'physical' picture of the atom, something can be said about the relation between the two. In brief, our claims come down to the following:

- (i) The 'chemical' and the 'physical' conception of the atom will lead to only one formalization of the Periodic Table, in which the meaning of the relevant terms differs, but the structures created (the potential models) are essentially the same, i.e., they are isomorphic. In the 'chemical' picture of the atom for instance, 'chemical similarity', includes 'having the same valency', while in the 'physical' picture, 'chemical similarity' can be related to similarities in the 'outer electron configuration'. (This means automatically that also the concept of 'valency' itself can be related to 'outer electron configuration'.)
- (ii) By making use of Atomic Theory, the sophisticated Periodic Law can be 'explained'.

First, we will make clear what is meant by the term 'Atomic Theory'. As can be expected, Atomic Theory will take the 'physical' conception of the atom as its starting point. In Section 4.1 it is said that the 'physical' conception of the atom, for its description of atoms, uses quantum theory. Atomic Theory itself mainly consists of the application of quantum theory to 'atomic systems', taken together with a set of possible approximations we mentioned in the last subsection.

There we also made the statement that these approximations can be used in such a way, that it becomes hard to continue talking about 'quantum theory'. Therefore we will prefer to talk about 'concepts of quantization' instead of quantum theory.

The most simple theory that describes atomic behaviour and uses

concepts of quantization, is the Bohr theory of the atom. This theory was originally intended to describe the behaviour of the electron cloud in a 'physical' way, by fixing attention to the explanation of atomic spectra. Its off-spin was the explanation of the Periodic Table. Hence, we will treat the Bohr theory, despite its level of approximation, as being a *physical* theory. In this sense, it forms an example for more sophisticated versions of Atomic Theory. So, on the basis of this theory, the terms used in Df. 1 can be given a new interpretation.

The set E , which denoted in our former definition the set of chemical elements, now denotes the set of systems with each one nucleus, and one or more electrons. The atomic number function z now indicates the number of protons in the nucleus or, equivalently, the number of electrons involved (when dealing with an electrically neutral system). The mass function m now denotes the total mass of each system $e \in E$, expressed in $1/12$ of the mass of ^{12}C . Finally, the relation \sim now indicates the relation of having the same 'valence electron configuration', this means that two elements stand in the relation \sim e.g., when both have a d^3 configuration. All groups, occurring in the Periodic Table, can be identified with some sort of 'outer electron configuration'.

Working with this model and keeping proper track of the angular momentum, the factor $2n^2$ in the sophisticated Periodic Law (SPL) can be explained by correlating n to the principal quantum number. A full treatment of the quantum theory of atoms can be found in any textbook on the subject of quantum mechanics and quantum chemistry. For detailed quantum mechanical discussions of the Periodic Table one can consult for instance Dash (1968) or Gasiorowicz (1974).

For our purposes, it is sufficient to conclude, that the relation between Atomic Theory and the Periodic Table consists of two parts:

- (i) Atomic Theory is able to define the terms of the Periodic Table on an ontologically deeper level: all terms are expressed in terms of the 'physical' conception of the atom. Especially the term z , which in the original version of the Periodic Table only plays the role of an ordinal number, is in this way given a more fundamental meaning, it represents the number of electrons involved in a neutral atom.

- (ii) The Periodic Law SPL can be explained, using Atomic Theory.

4.3. *A case of reduction*

More or less as a side-step, we will argue that, according to a recent, informal general diagnosis (Kuipers, 1987, 1988), the present explanation is to be counted as an interesting example of a reductive explanation or, simply, a reduction. The general analysis starts with the claim that any explanation of a law by a theory can be decomposed into one or more of the following five steps: *application* of the theory to the kind of object where the law is about, *aggregation* of the individual result over the relevant totality of objects, *identification* of theory-terms with law-terms, on the basis of some identity hypotheses, (causal) *correlation* of theory- or identified terms with law-terms on the basis of some causal hypotheses and *approximation* of the result by a simplified version on the basis of some counterfactual idealizational hypotheses. It will be clear that identification as well as correlation lend to a *transformation* of the result obtained in the foregoing step.

The diagnosis states that explanations are called reductions, at least by leading philosophers of science, as soon as at least one of the following three steps is involved in the explanation (in a non-trivial way): aggregation, identification and approximation. Now it is clear that there is in the explanation of SPL, beside trivial mass-aggregation and -identification, the non-trivial identification of atomic number and number of electrons. Hence, it is a reduction. It is a particularly interesting example for the following reason. The necessary link between chemical similarity and equal outer electron configuration states that the later *causes* the former. Hence, this link is no identification but (only) a causal correlation. The fact that both types of transformation (identification and correlation) occur simultaneously makes the example an interesting example of explanation, for one might think that correlation cannot go together with identification, but at most follow after identification. To be more precise, one might think that it is only possible to have identification of a theory-term with some 'intermediate' term, followed by correlation of the latter with a law-term. However, the present example shows that it is possible to have identification of some theory-term with some law-

term, and at the same time correlation of some other theory-term with some other law-term.

5. IS THE PERIODIC TABLE A THEORY?

Up to this point, we have presented the Periodic Table as a theory, having its own theoretical term, intended application, and central law. In this section, we will raise the question whether the Periodic Table can be viewed as a theory. Most books on the subject of practical chemistry treat the Periodic Table as a *table* indeed, and do not mention the word 'theory'.

In his article 'Scientific theories and their domains' Shapere has taken the view that the Periodic Table is an *ordered domain* 'that is, domains in which types of items are classified', but certainly not a theory: 'Nor does the fact that the ordering sometimes allows predictions to be made (...) turn such ordered domains into theories' (see Shapere, 1974). Much of his argument has to do with the Periodic Law being some sort of ordering principle, that, after the ordering has been established, becomes part of the domain itself.

We like to discuss these matters in terms of the sophisticated distinction between *empirical laws* and *proper theories* as developed elsewhere (Kuipers and Zandvoort, 1985). Our conclusion will be that the Periodic Table was a proper theory from Mendeleev's point of view, that the sophisticated one would also be a proper theory if we neglect the Atomic Theory, but that, in view of the Atomic Theory, it is in principle an empirical law (to be precise: a quasi-law).

The general distinction between empirical laws and proper theories can be introduced as follows. We start with some structuralist definitions: the naive one for theories and the pragmatic one for theoricity. A *theory* is a triple $T = \langle M_p, M, I \rangle$, where M_p is a class of potential models, M the class of models and I an M_p -description of the set of intended applications (hence $I \subseteq M_p$). A term of T , i.e., a term occurring in M_p -structures, is *T-theoretical* or *laden with T* if every (existing or at least well-conceivable) method of measurement presupposes the (partial) validity of the claim $I \subseteq M$, it is *T-non-theoretical* if this is not the case. Note that this distinction has nothing to do with purely observational or theory-free terms: as a rule, a term not laden with T is nevertheless laden with other, underlying theories.

A theory T is a *proper theory* if it has at least one T -theoretical term,

it is an *empirical law* (in the strict sense) if it has none. Hence, an empirical law is an improper theory, i.e., a theory without own theoretical terms. According to these definitions Galilei's law of free fall and Kepler's laws of planetary motion are easily seen to be empirical laws, if we neglect the constants occurring in them for a moment, whereas Newton's theory of motion is a proper theory. The ideal gas law ($PV = RT$) is a nice example illustrating the necessity of an important refinement of the distinction. Strictly speaking, R and T in $PV = RT$ are laden with $PV = RT$, hence $PV = RT$ would count according to the above definition as a proper theory, which deviates from common practice. Fortunately, there can be formulated three empirical laws in the strict sense given above, which enable the explicit definition of R and T . With this definition the conjunction of the three laws is equivalent to the ideal gas law (see Kuipers, 1982). It is easy to check that the constants occurring in the laws of Galilei and Kepler can also be defined in a similar, though more trivial, explicit way.

The lesson is of course the following revised definition: A theory T is an *empirical law* if it is an empirical law in the strict sense *or* if its ostensible theoretical terms can be defined explicitly on the basis of empirical laws in the strict sense. In the last case such terms are said to be improper theoretical terms, as opposed to proper ones. Hence, a proper theory has proper theoretical terms, whereas an empirical law does not have such terms. Note, by the way, that one of the original logical empiricist's intentions can now be stated as follows: they wanted to leave room for theoretical terms only if they are improper in our sense. Our apparent intention to leave room for proper theoretical terms is indeed turning this original intention upside down.

Now let us turn to the evaluation of the Periodic Table. We begin with the naive table or theory:

$$NPT =_{df} \langle M_p(PT), M(NPT), \langle E, m_E, \sim_E, z_E \rangle \rangle.$$

Our claim is that z is a proper theoretical function in NPT and hence that NPT is a proper theory. The reason is, paradoxically enough, that Mendeleev was willing to admit that global satisfaction of the naive empirical claim at least required the acceptance of some local exceptions. To put it differently, if Mendeleev would have had easy access to E and if there would have been no reason for exceptions, then z would simply be a bijection on $\{1, 2, \dots, |e|\}$, reflecting the mass-ordering. In that case it would be possible to define z explicitly and

NPL, or better, NPT would be an empirical law. However, not all members of E were available to Mendeleev and he placed the available elements in the Table by presupposing the validity of the relevant part of NPL, leaving room for existential exceptions. If Mendeleev would have discovered, in addition, that it is necessary to admit isotopes and (other) order exceptions, in order to save NPL, z would have become theoretical also in these respects.

Later it has been discovered that NPL cannot be saved in this way, i.e. that, in addition to local exceptions, some systematic deviations turn out to be unavoidable. The sophisticated table or theory SPT, obtained from the definition of NPT by replacing 'M(NPT)' by 'M(SPT)', meets these problems of NPT.

Now it is easy to see that, as long as we neglect the Atomic Theory (AT), the evaluation of SPT is the same as that of NPT: it is also a proper theory exactly because of the required recognition of local exceptions.

However, SPL, and hence SPT, were formulated along with the development of AT, where the atomic number function z obtained the interpretation of the number of electrons. Hence, the question is whether AT led to new ways of measurement of z independent of SPT. The answer is a qualified YES. To be sure, z is within AT a theoretical term: However, although AT explains SPT, it leaves room for ways of measurement of z , dependent on AT, but independent of SPT, of course in the sense of 'AT-laden' measurement of the number of electrons, and presupposing the identification of this number with z . Although in actual practice AT and SPT are *de facto* interwoven in the measurement of z , it is clear from AT that the number of electrons could be counted in an SPT-free way, by registering successive 'stripping' of electrons from a neutral atom. Hence, in contrast to NPT, SPT can be conceived as an empirical law, namely if it is viewed in the light of AT, and the identification of z with the number of electrons: for, in principle or *de jure*, all terms of SPT can be measured independently from SPT, which is, by our previous definition, the condition for calling it an empirical law. Note that AT (together with the identification bridge principle) functions in this *de jure* line of thought as a measure theory for SPT.

Coming back to Shapere, it is clear that his claim reads in our terms that the Periodic Table is an empirical law. With some plausible definitions we have arrived at the conclusion that it was a proper

theory for Mendeleev, and that (the sophisticated version of) the Table became only an empirical law due to the Atomic Theory.

It is interesting to note that the change of status parallels the transition of z from an instrumentalist function in the naive Table to a (relatively) realistic notion in the Atomic Theory interpretation of the sophisticated Table. We are not sure whether these two transitions always go together.

Be this as it may, it is certainly not the case that the change of status has something to do with the fact that the Atomic Theory deals with an ontologically deeper level.

What is clear, however, is that the Periodic Table is a nice example of a theory that starts as a proper theory which turns at least *de jure* into an empirical law by underpinning it with another, epistemologically independent, proper theory (which happens to be ontologically deeper). The theoretical character of certain terms in the former, proper theory is taken over by terms of (or can perhaps be dissolved in other cases by) the new one, which becomes *de jure* an (epistemologically) underlying measure theory of the resulting empirical law. Of course, the fact that the measurement of z is usually *de facto* laden with the (sophisticated) Periodic Table and hence that the latter should therefore *de facto* be conceived as a proper theory, nicely illustrates that the *de jure* epistemological status of a theory may differ from its *de facto* status.

NOTE

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